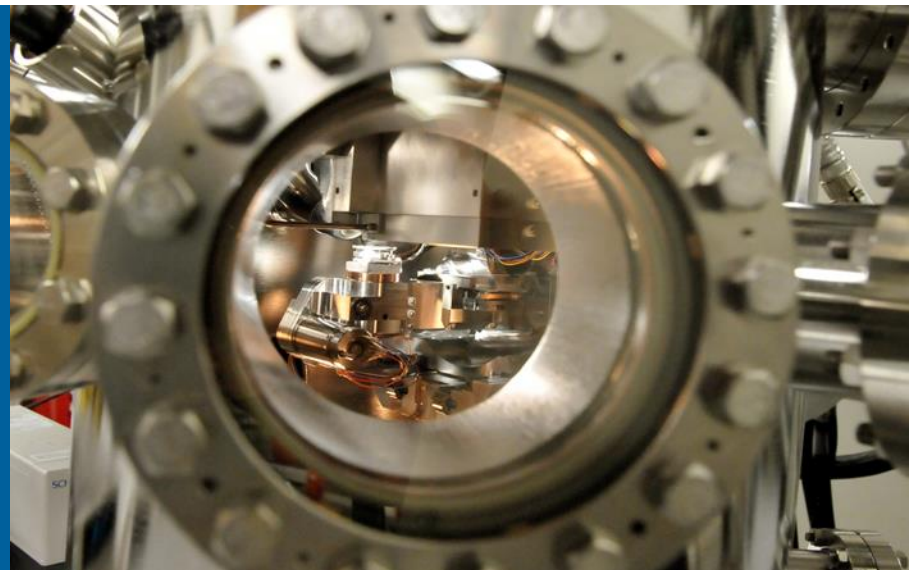


POST-TEST ANALYSIS OF LITHIUM-ION BATTERY MATERIALS

Effect of electrode cross-talk



N. DIETZ RAGO, J. BAREÑO
I. BLOOM



D. WOOD, Z. DU, Y. SHENG,
JIANLIN LI



K. FENTON, L. A. STEELE, J. LAMB,
S. SPANGLER, C. GROSSO



DOE Annual Merit Review
Washington, DC, June 18-21, 2018

This presentation does not contain any proprietary, confidential or otherwise restricted information

PROJECT ID: BAT166

OVERVIEW

TIMELINE

- Project start: October 1, 2015
- Project end: September 30, 2018
 - 67% complete

BUDGET

- FY18:
 - ANL-\$850K (expected), \$400K (received)
 - SNL-\$190K(expected), \$0 (received)
 - ORNL-\$200K (expected), \$180K(received)
- FY17: \$850K
- FY16: \$750K

OBJECTIVES

- Barriers addressed: performance, life and abuse response
- Elucidate physical and chemical response of constituent battery materials under battery abuse conditions
- Develop analysis procedures

COLLABORATORS

- Oak Ridge National Laboratory
- Sandia National Laboratory
- NEAH Power

RELEVANCE

Science Issues/Objectives

Investigate the following:

- Impact of processing methods on the performance of the cells.
- Effect of type of binder and drying procedure on the SEI layer, cell impedance, binder degradation, gases, and current collector corrosion.
- The underlying changes in cell components during an abuse event, such as overcharge.
 - Are there effects from battery format? Chemistry?
 - How do these effects manifest themselves?

In principle, we can use what we learn to mitigate the effect of abuse

MILESTONES

Milestone	Due date	Type	Status
Compare aqueous- and organic-processed electrode, elucidating differences.	9/30/16	Annual SMART milestone	Delayed. Initial comparison showed a difference in reactivity
Compare pre- and post-abuse event cell materials, elucidating changes in electrode materials	9/30/17	Annual SMART milestone	Complete. See the three attached manuscripts also.
Anode and cathode SEI characterization Complete anode and cathode SEI layer characterization of NMC811/Si-C single-layer 100-mAh pouch cells produced via aqueous processing with baseline and optimized formation protocol (after formation and at least 100 1C/-2C cycles).	9/30/18	Annual SMART milestone	

APPROACH

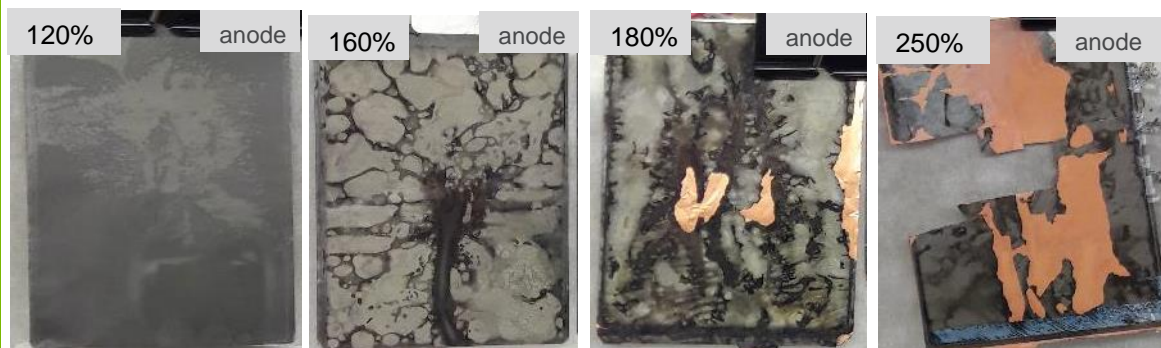
As part of our larger study in the systematic overcharge of electrodes with different chemistries, binders and formation protocols, we compared two different cathode chemistries, NMC and LFP, that were formulated using PVdF as the binder. We investigated how electrode cross-talk changes abuse response

- Pouch cells based on NMC523/graphite and LFP/graphite chemistry were fabricated by ORNL
- At SNL, the cells were charged to 100, 120, 140, 160, 180, 250% state of charge and discharged to ~0% SOC before shipment to ANL
- The cells were then taken apart to determine the physical and chemical changes that took place during the charging events.

TECHNICAL ACCOMPLISHMENTS & PROGRESS

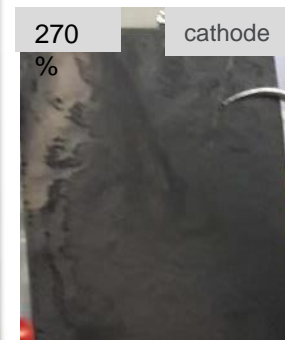
Anode changes are sensitive to the cathode

NMC/Graphite cell



NMC cathode shows more delamination at failure than LFP cathode

LFP/Graphite cell

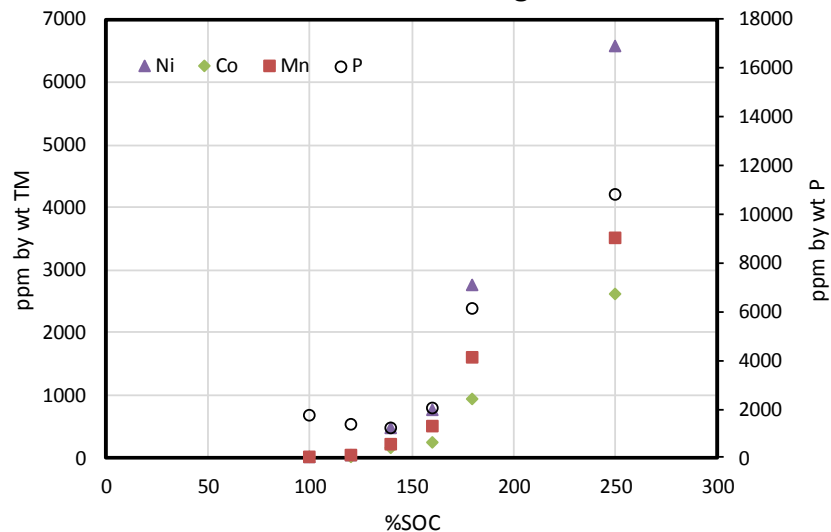


LFP cathode shows discoloration and delamination at failure.

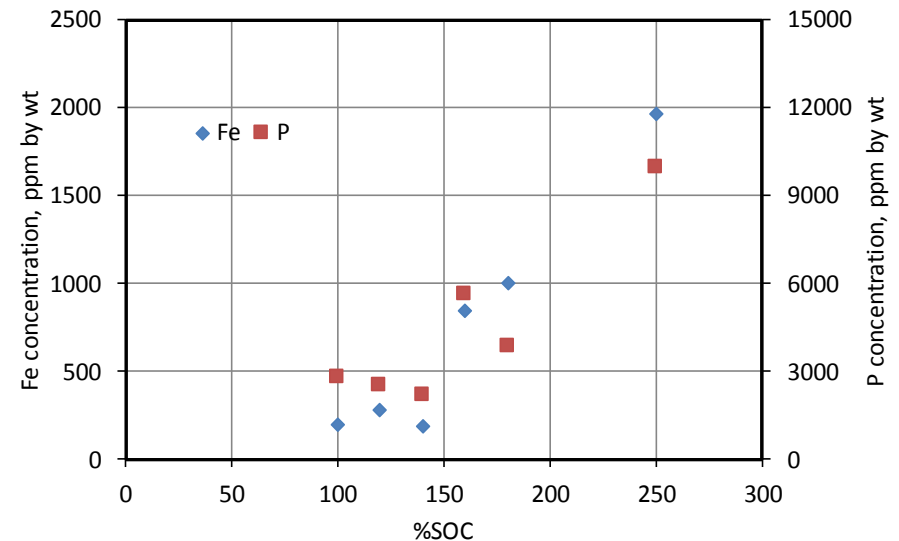
- The NMC anode surfaces have more discoloration with increasing SOC than the LFP anode surface. SEM analysis reveals that the discoloration is associated with increasing superficial reaction products.
- The NMC anodes show more delamination than the LFP anodes.

METAL MIGRATION FROM CATHODE TO ANODE INCREASES WITH STATE OF CHARGE

NMC/Graphite



LFP/Graphite



- **NMC:** Migration of transition metals follows stoichiometry (Ni:Mn:Co ~5:3:2)
- **LFP:** Migration of Fe and P increases with increasing SOC

HPLC RESULTS PROVIDE INFORMATION REGARDING COMPOSITION OF ANODE SEI LAYER

Composition depends on cathode

- **NMC:** Two peaks in total-ion chromatogram (TIC) showed dependence on SOC

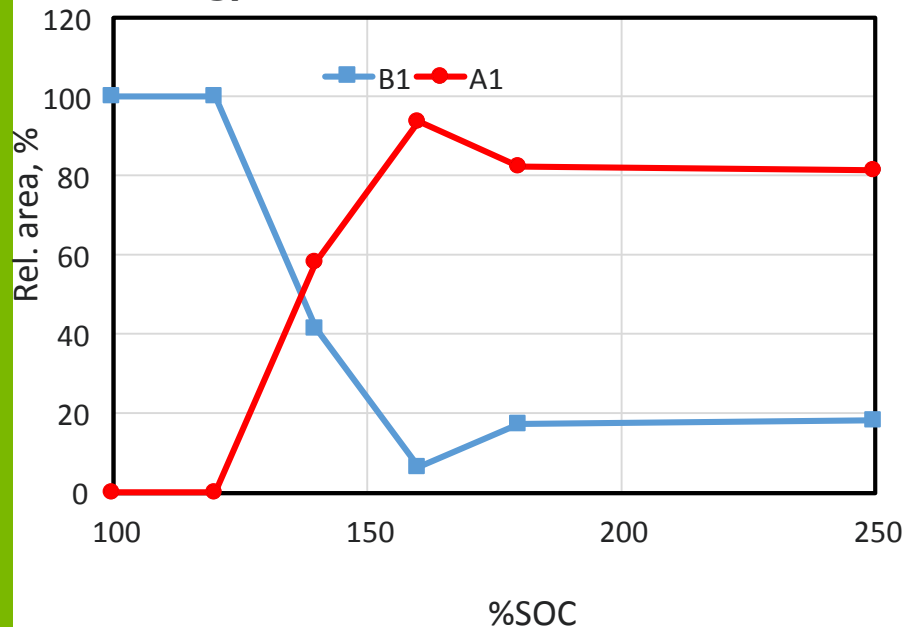
Retention time, min	Label	Found m/e, Da	Estimated number of carbons (avg)
2.76	A1	419	17.6
6.53	B1	445	12.7

- **LFP:** Four peaks in TIC showed dependence on SOC

Retention time, min	Label	Found m/e, Da	Estimated number of carbons (avg)
2.35	A2	431	15.2
2.83	B2	431	15.5
3.62	C2	381	16.6
6.13	D2	307	15.0

DEPENDENCE OF SEI COMPONENTS WITH OVERCHARGE

NMC/NMP

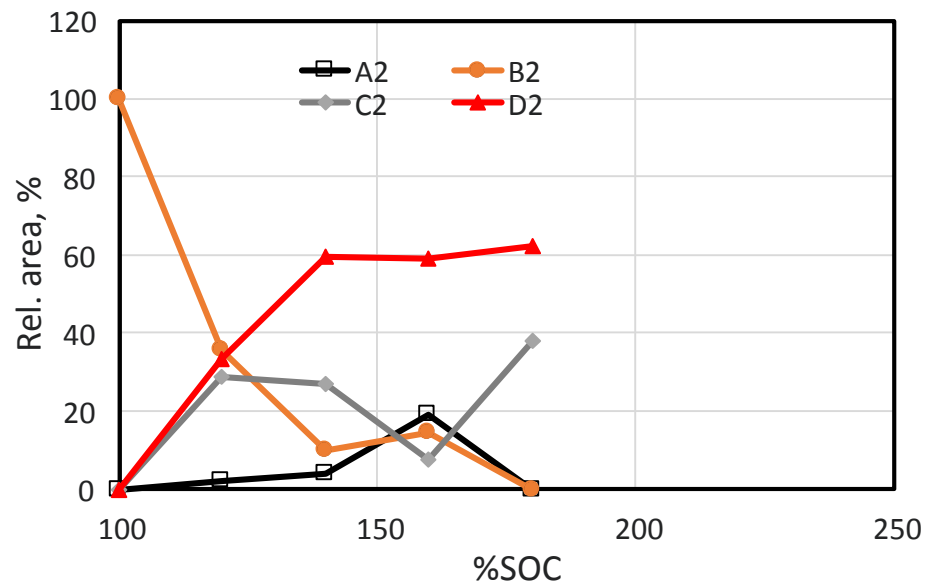


- Peak B2 declined with %SOC, while others tended to grow. As %SOC increased past 140%, Peaks C2 and D2 tended to reach a steady state

- At low values of %SOC, only Peak B1 was observed. As %SOC increased past 120%, Peak A1 grew in and Peak B1 decreased. The peaks then were present in a constant area ratio, ~4.5:1

LFP/NMP*

Different peaks were present



PROPOSED COMPOUNDS FROM HPLC DATA (1)

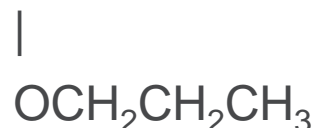
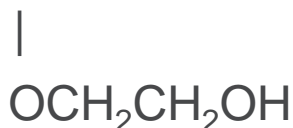
NMC/NMP

- **A1** (investigate compounds with 16-19 carbons):

$[\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OP}(=\text{O})(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3)_2 \cdot \text{H}^+]$ (FW: 419.4 g/mol)

- **B1** (11-14 carbons):

$[\text{HOCH}_2\text{CH}_2\text{OP}(=\text{O})\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OP}(=\text{O})\text{OC}_2\text{H}_5 \cdot \text{H}^+]$ (FW: 422.3 g/mol)



LFP/NMP

- **A2** (14-17 carbons):

$[(\text{HOCH}_2\text{CH}_2\text{OCH}=\text{CHO})_2\text{P}(=\text{O})\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5 \cdot \text{H}^+]$
(FW=431.4 g/mol)

- **B2** (14-17 carbons): since the retention time and carbon count are similar to those of A2, B2 could be an isomer of A2.

- **C2** (15-18 carbons): $[\text{CH}_3\text{OCH}=\text{CHO}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}=\text{CHO}(\text{CH}_2\text{CH}_2\text{O})_4\text{H} \cdot \text{H}^+]$
(FW=381.4 g/mol)

- **D2** (13-17 carbons): $[\text{CH}_3\text{OCH}=\text{CHO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}=\text{CHOCH}_2\text{CH}_2\text{OCH}_3 \cdot \text{H}^+]$
(FW=307.4 g/mol)

PROPOSED COMPOUNDS FROM HPLC DATA (2)

Assuming that the species proposed are indicative...

- More species were detected in the LFP case than in the NMC, indicating different reaction pathways may be available in the former.
- Both cell types display organophosphates/-ites as possible surface species.
- The side chains on them are similar, but the LFP case may have unsaturated side chains.
- Additionally, the other compounds in the LFP case may be unsaturated polyethers formed from EC and LiPF_6 decomposition products.

such as:

$\text{EC} + 2\text{e}^- + 2\text{Li}^+ \rightarrow \text{LiCH}_2\text{CH}_2\text{OCO}_2\text{Li}$, which can lose CO_2 and polymerize¹

$\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{HF} + \text{PF}_5$

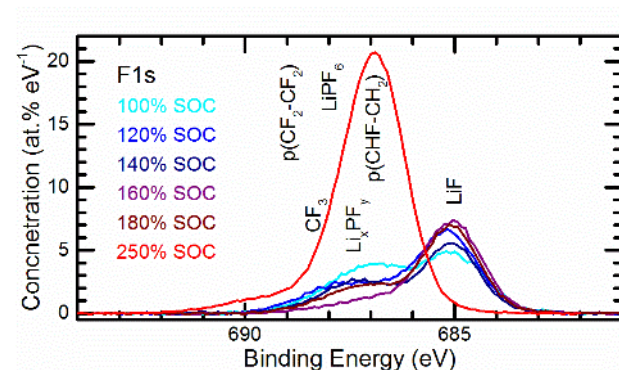
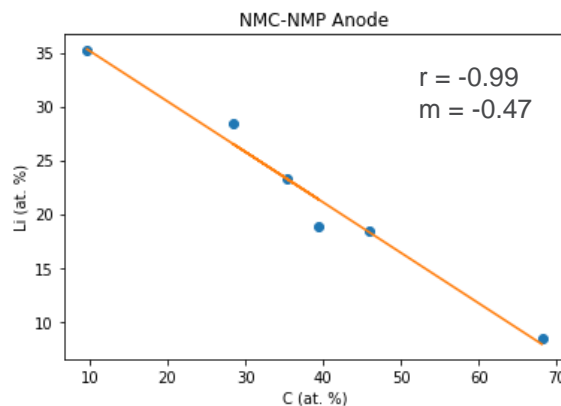
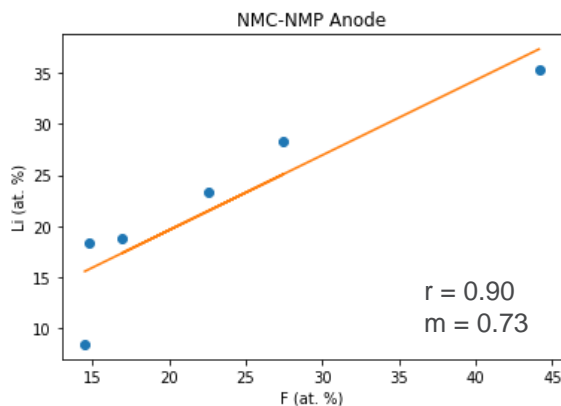
$\text{PF}_5 + \text{EC decomposition products} \rightarrow \text{organophosphates/-ites}$

- Together, these may indicate that the NMC cathode fosters the production of more phosphorus-bearing intermediates than LFP.

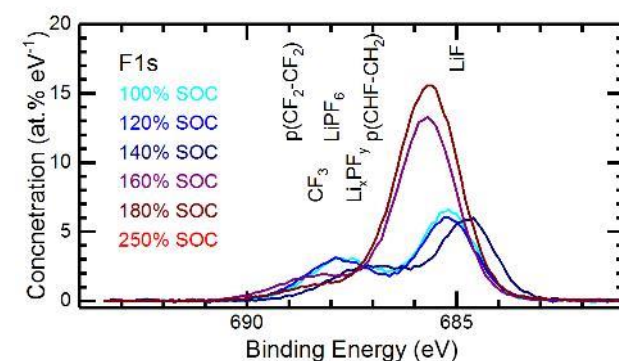
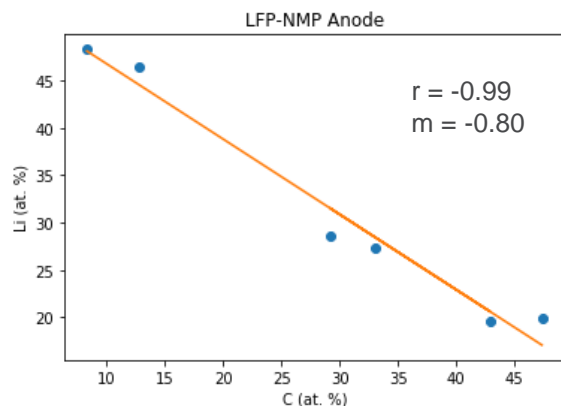
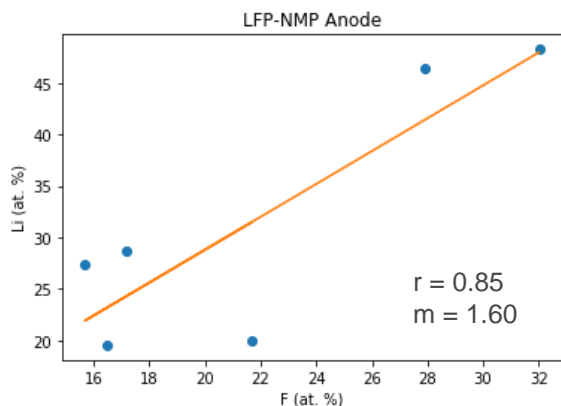
¹D. Aurbach, A. Zaban, Y. Ein-Eli, I. Weissman, O. Chusid, B. Markovsky, M. Levi, E. Levi, A. Schechter, and E. Granot, J. Power Sources, 68 (1997) 91–98.

POSSIBLE LIF-CONTAINING SEI FORMED ON ANODES

NMC



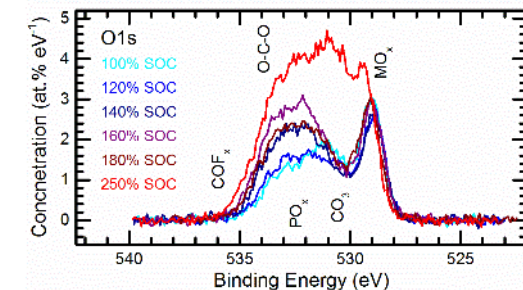
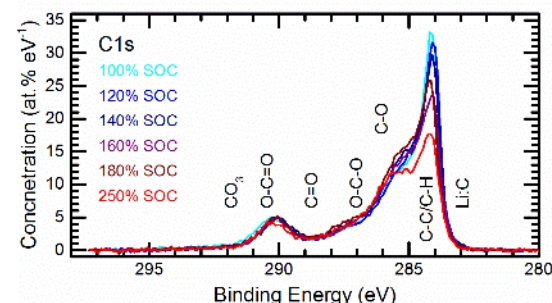
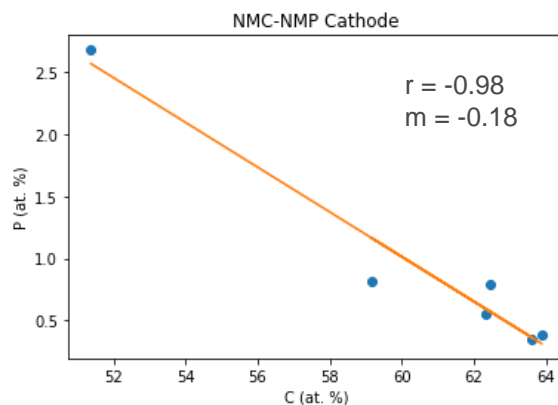
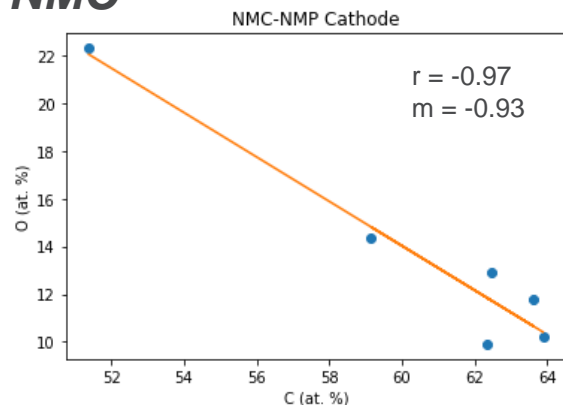
LFP



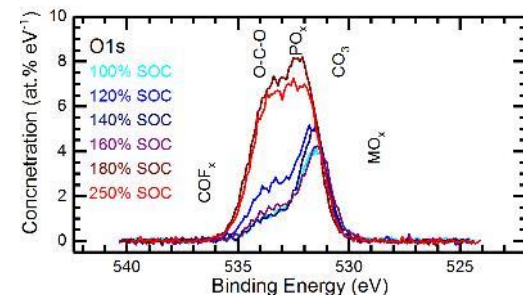
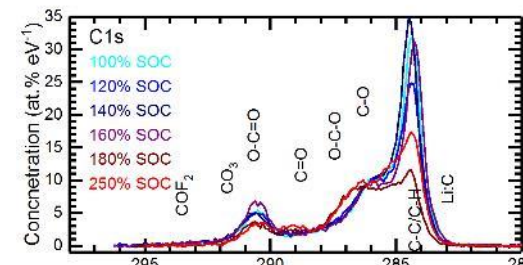
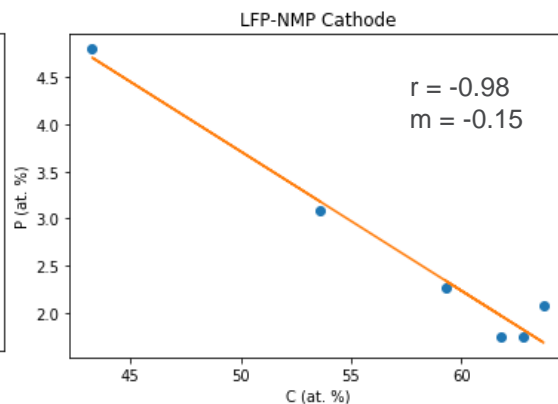
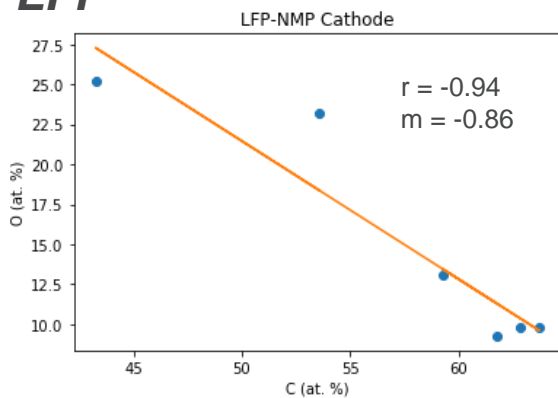
- Li shows strong linear correlation to F and anticorrelation to C on both anodes of the LFP and NMC cells.

ORGANICS APPEAR TO COVER CATHODES

NMC



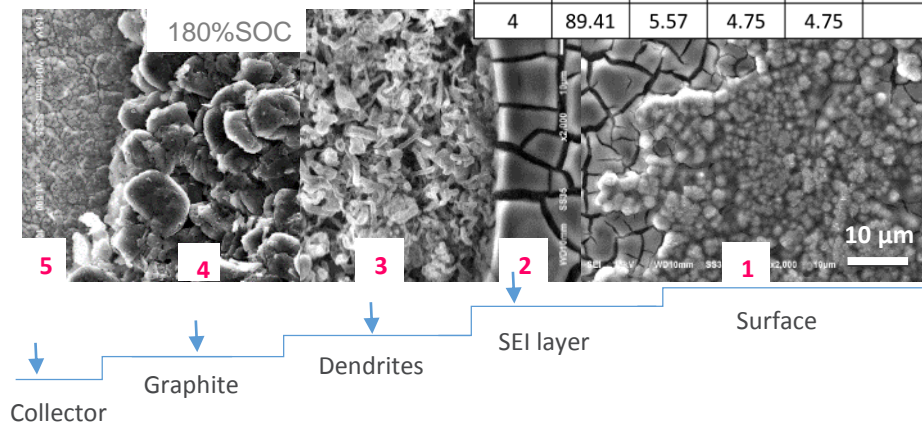
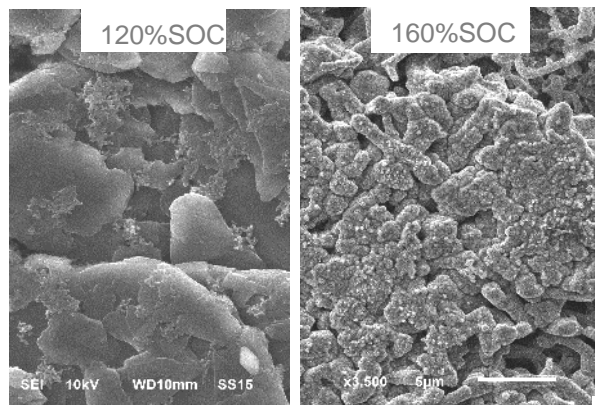
LFP



- Both O and P show strong linear anticorrelation with C, suggesting the growth of an organic layer covering the oxide LFP and NMC cathode materials

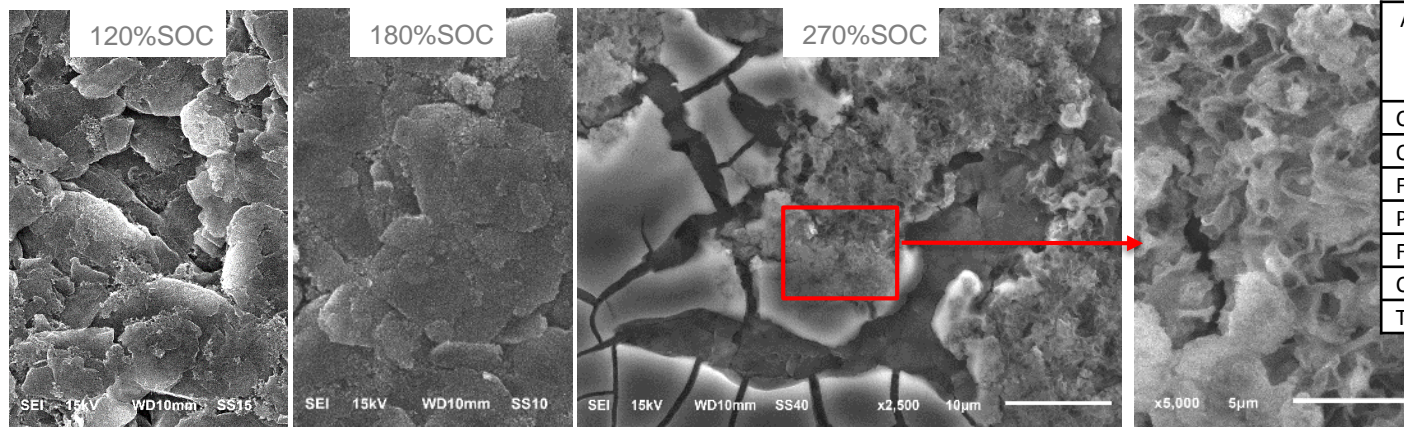
MICROSTRUCTURE OF ANODE SURFACE DEPENDS ON CATHODE (1)

NMC



area	C	O	F	P	S	Mn	Co	Ni	Cu
1	42.25	32.48	11.45	2.06	0.13	0.96	3.76	6.69	
2	23.63	14.44	54.37	6.06	0.33	0.37	0.25	0.70	
3	45.09	32.48	9.50	1.65	1.20	1.20	3.33	6.28	
4	89.41	5.57	4.75	4.75					0.05

LFP

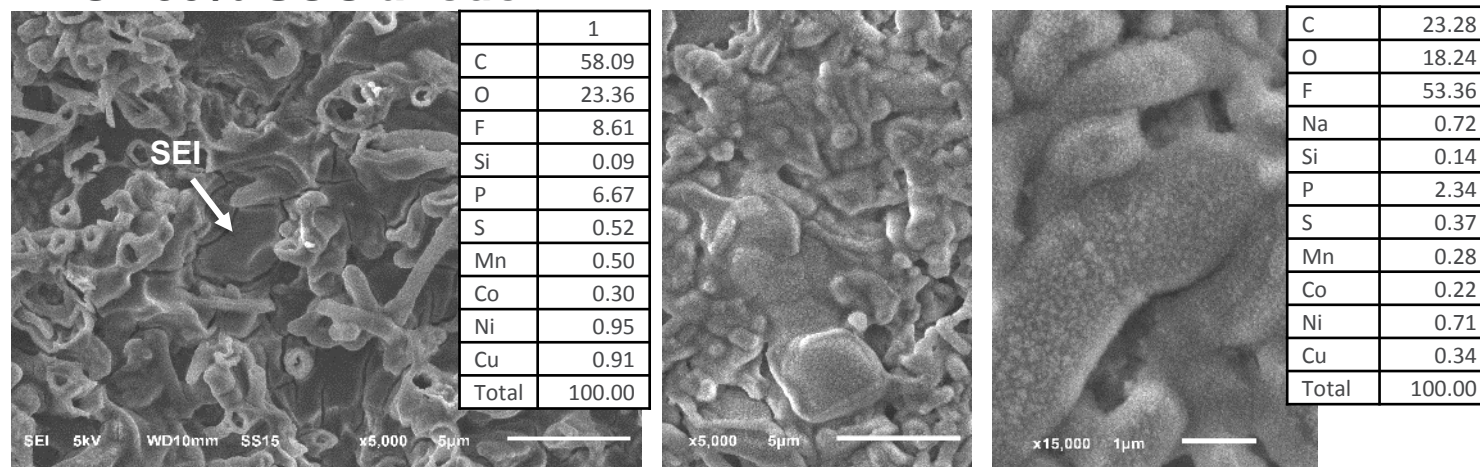


At %	120% FOV 1K	180% FOV 1K	270% FOV 4K
C	93.25	89.73	30.87
O	3.84	2.74	23.37
F	2.71	7.32	41.12
P	0.19	0.22	4.17
Fe			0.46
Cu			0.01
Total	100.0	100.0	100.0

- **NMC:** Anode surface has increasingly dense dendrite concentration and complex multi-layer structures. Highest concentration of TMs is associated with the dendrite layer (3) and surface (1).
- **LFP:** Surface develops an amorphous film seen at 180% SOC. EDS indicates F increases with increasing SOC and is associated with film formation. At 270% SOC, the film appears to be undergoing a transformation to dendritic growth (boxed area). Trace Fe is detected on the surface.

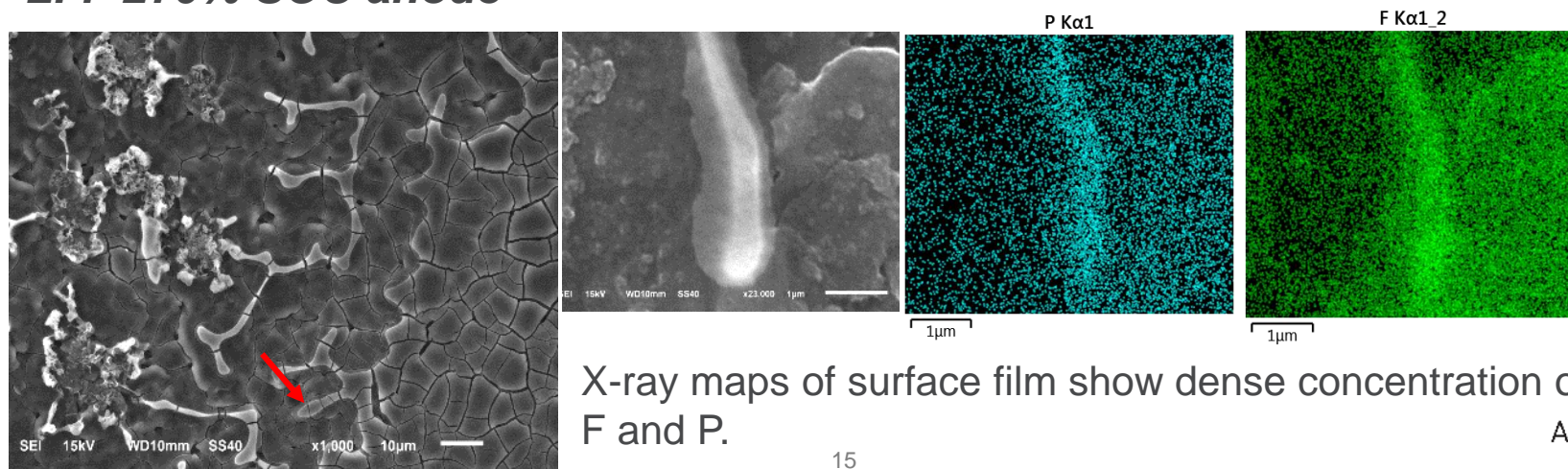
MICROSTRUCTURE OF ANODE SURFACE DEPENDS ON CATHODE (2)

NMC 250% SOC anode



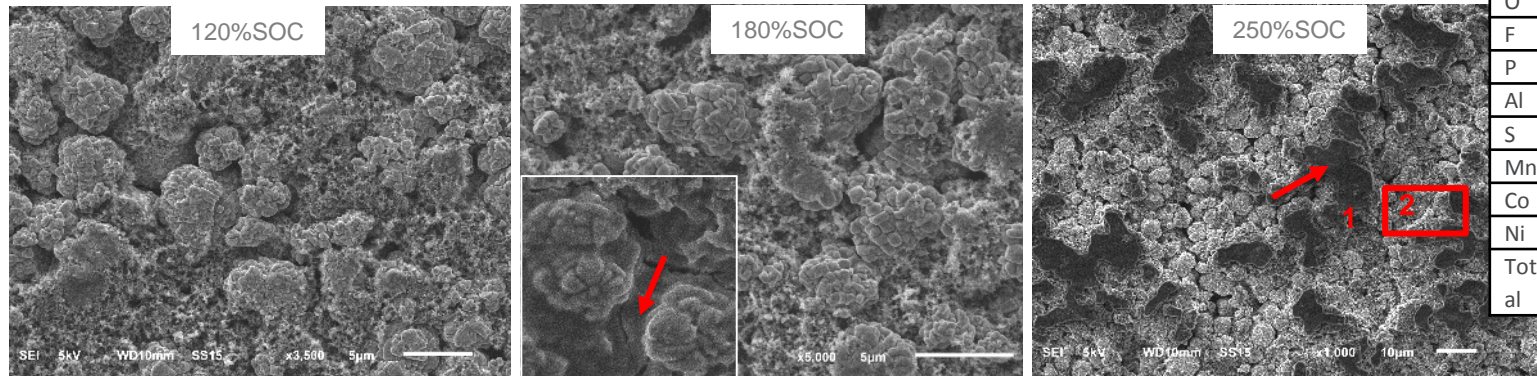
Surface is heavily coated with dendrites that contain trace TMs. First image shows area on surface that had pull-out onto the separator during disassembly, exposing the SEI layer and newly formed smooth dendrites. TMs are detected in the SEI and in the dendrite coating.

LFP 270% SOC anode



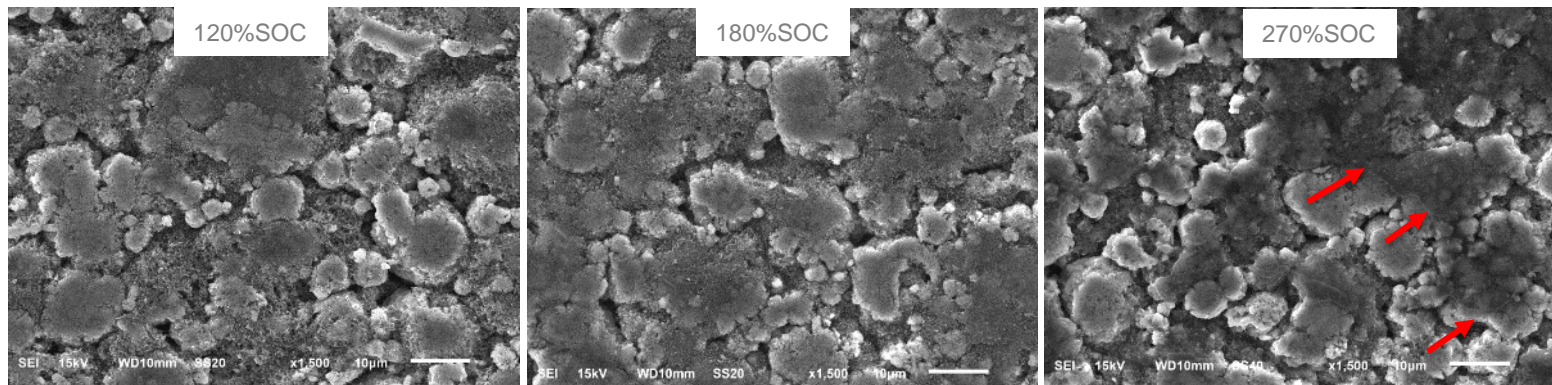
MICROSTRUCTURE OF CATHODE SURFACE DEPENDS ON SOC

NMC Cathode



	1	2
C	59.25	47.08
O	14.86	31.19
F	18.91	6.50
P	1.79	0.06
Al		0.03
S	0.07	
Mn	1.38	4.95
Co	0.98	3.04
Ni	2.77	7.15
Tot al	100.0	100.0

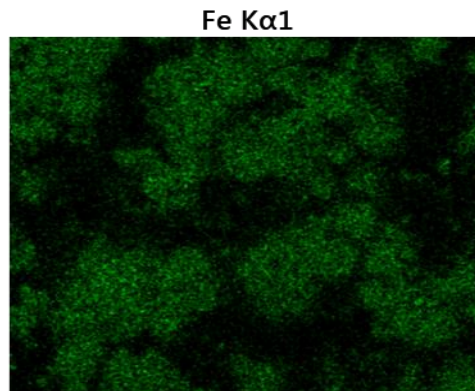
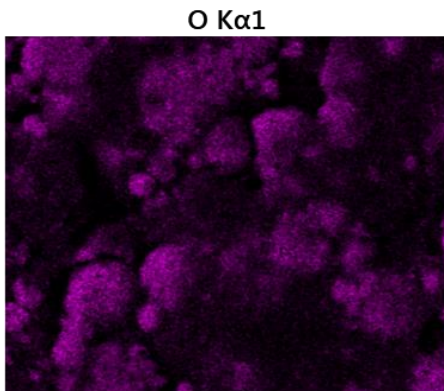
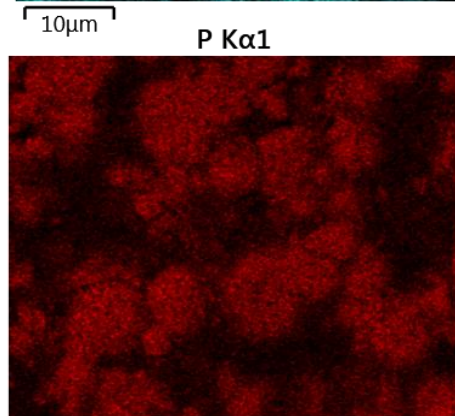
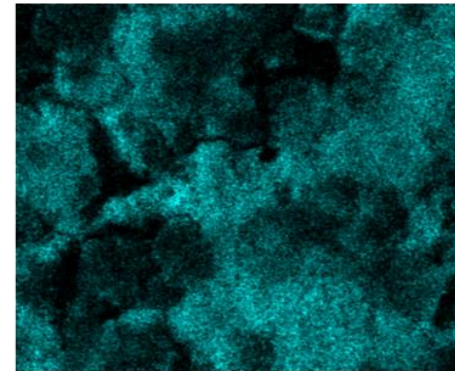
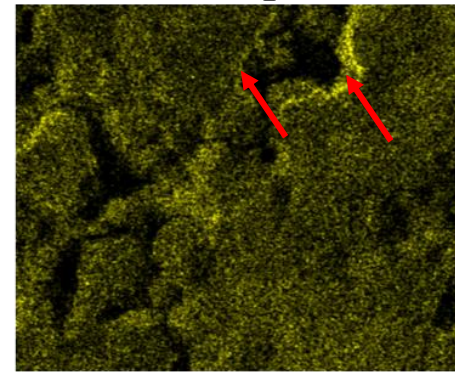
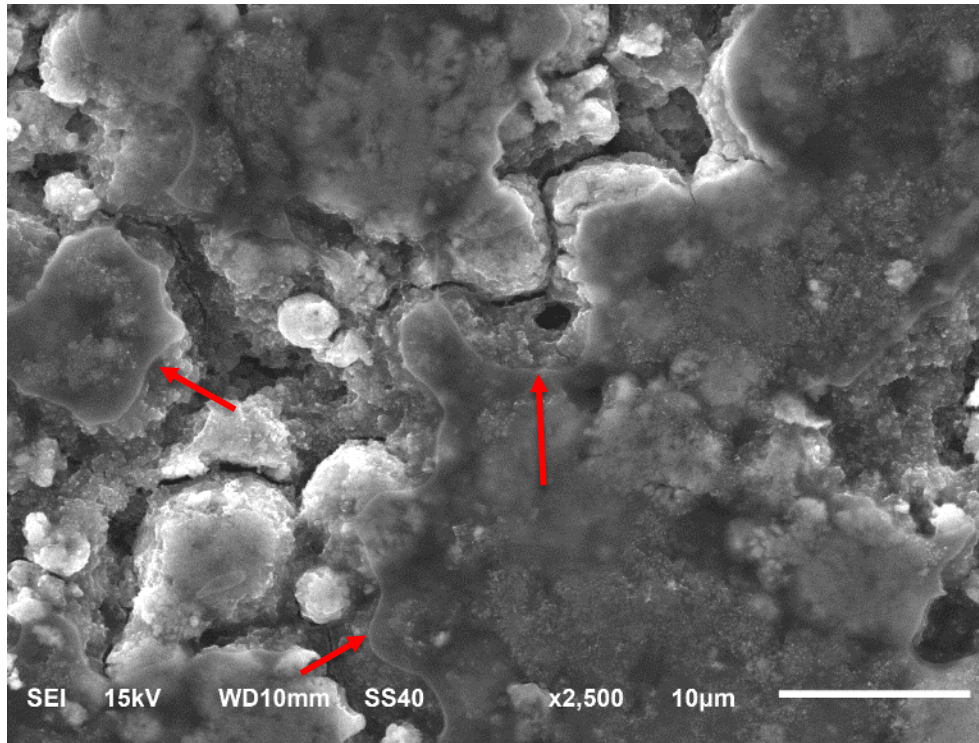
LFP cathode



The surface microstructures in both cathodes appear unchanged until 180% SOC.

- **NMC:** Amorphous material between particles has formed in some areas at 180% SOC (inset). More topographic variation is present starting at 180% SOC suggesting a loss of binder. Superficial dark regions of amorphous material are high in F and P (arrows).
- **LFP:** A surface film appears at 180% SOC and has grown by 270% SOC (arrows).

X-RAY MAPS SHOW F-RICH DISCONTINUOUS FILM ON SURFACE OF LFP CATHODE



REVIEWERS COMMENTS

AMR 2017

- The reviewer commented that only one type of abuse tests (i.e., overcharge) was performed. The work can be improved by leveraging Sandia National Laboratories (SNL) facilities and performing more types of abuse tests (e.g., thermal and mechanical abuse tests).

Response: Future work will investigate changes in high-energy cells with thermal abuse.

- It seems useful, but it was unclear to the reviewer how knowing the various responses to abuse will help make safer batteries. The reviewer further noted that the project team will test different additives, but again, was unsure how looking at morphology changes will add knowledge.

Response: We not only study morphological changes, we also use several analytical methods, such as ICP-MS, HPLC, XPS, XRD and Raman/IR, to measure chemical and structural changes as well. The knowledge gained from these analyses helps us understand reaction mechanisms of the abuse response that in turn allows us to mitigate the undesirable reactions by tailoring the chemistry and/or structure of the cell, whether through additives, coatings or changes in electrolyte, binder or **active** material chemistry/structure.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

A Three-laboratory consortium

- Argonne, Sandia and Oak Ridge teamed to leverage strengths and abilities at each site to study effects of processing and abuse response of two lithium-ion battery chemistries, high-Ni NMC and LiFePO_4
- What each site contributes
 - Argonne: Post-test Facility – ability to characterize battery materials under inert atmosphere
 - Sandia: Battery Abuse Testing Lab (BATLab) – ability to thermally and electrically abuse cells under controlled conditions
 - Oak Ridge: Battery Manufacturing R&D Facility – ability to make cells with well-defined chemistries, as the project needs



FUTURE WORK

- Investigate changes in high-energy cells with thermal abuse. Extend this work to Si/graphite electrode-containing cells. Include electrode cross-talk effects on response.
- Compare cells made with pristine materials with those made from recycled materials.
Do the physical properties of the electrode materials change after recycling?
Surface chemistry? Morphology?
- In the Xcel-15 project, determine smallest lithium deposit that can be seen using microscopy.
- Characterize cells that were aged at Argonne and those from Idaho, looking for the effects of fast charging and/or lithium plating.

ACKNOWLEDGMENT

We gratefully acknowledge the support from the US Department of Energy, Office of Vehicle Technologies— Peter Faguy and Dave Howell.

Any proposed future work is subject to change based on funding levels

SUMMARY

- LFP cell appears more stable than NMC cell
 - More discoloration on anode surfaces in NMP cell – evidence of surface reactions
 - More delamination from the collector in the NMC cell anode
- Starting at 100% SOC, dissolution of metals from both types of cathodes and subsequent migration to the anode surface increases with higher states of charge.
- More organic species were detected in the LFP case than in the NMC, indicating different reaction pathways may be available in the former. Both cell types display organophosphates/-ites as possible surface species. The side chains on them may be similar, but the LFP case may have unsaturated side chains.
- Microstructure of the anode surface depends on the cathode chemistry.
 - Dendrites formed on the NMC cell anode
 - An amorphous film formed on the LFP cell anode